

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : B01D 71/02	A1	(11) International Publication Number: WO 99/61140 (43) International Publication Date: 2 December 1999 (02.12.99)
(21) International Application Number: PCT/NL99/00333 (22) International Filing Date: 28 May 1999 (28.05.99) (30) Priority Data: 98201783.1 28 May 1998 (28.05.98) EP (71) Applicant (for all designated States except US): STICHTING ENERGIEONDERZOEK CENTRUM NEDERLAND [NL/NL]; Westerduinweg 3, NL-1755 LE Petten (NL). (72) Inventors; and (75) Inventors/Applicants (for US only): DE VOS, Renate, Marina [NL/NL]; Abersland 1126, NL-6605 MG Wijchen (NL). VERWEIJ, Hendrik [NL/NL]; Groenlandhorst 12, NL-7531 LG Enschede (NL). BONEKAMP, Benedictus, Clemens [NL/NL]; Mezenhof 28, NL-1742 GL Schagen (NL). PEX, Petrus, Paulus, Antonius, Catharina [NL/NL]; Wierbalg 2323, NL-1788 VG Den Helder (NL). (74) Agent: DE BRUIJN, Leendert, C.; Nederlandsch Octrooibureau, Scheveningsweg 82, P.O. Box 29720, NL-2502 LS The Hague (NL).		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: PROCESS OF PRODUCING A MICROPOROUS HYDROPHOBIC INORGANIC MEMBRANE (57) Abstract Microporous hydrophobic inorganic membrane having an average pore size of less than 2 nm and a hydrophobicity index octane/water of at least 2 can be obtained by a process comprising hydrolysing a metal alkoxide in the presence of a hydrocarbyl metal alkoxide having at least one non-hydrolysable group in an organic solvent to produce a metal (hydr)oxide sol, and precipitating metal (hydr)oxide from said sol and drying the precipitate. In this process, at least 50 % of the amount of hydrocarbyl metal alkoxide is introduced into the solvent after 20 % of the hydrolysis period has lapsed.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

Process of producing a microporous hydrophobic inorganic membrane

The invention relates to a process for producing a microporous hydrophobic inorganic membrane comprising hydrolysing a metal alkoxide in the presence of a hydrocarbyl metal alkoxide in an organic solvent to produce a metal (hydr)oxide sol, and precipitating metal (hydr)oxide from said sol and drying and calcining the precipitate.

Such a process for producing hybrid membranes has been described by Dirè et al, *J. Mater. Chem.*, 1997, 7, 67-73 and 919-922. These authors report the production of unsupported membranes by hydrolysing a mixture of tetraethoxysilane and methyltriethoxysilane in 70/30, 50/50 and 30/70 ratios at room temperature and at pH 1.5. The resulting sol was allowed to form a gel having a thickness of 10-40 µm and dried. Gas permeation for helium, nitrogen and argon was studied, and a selective permeation of helium to nitrogen was found, depending on the methyl content of the gel membrane. However, the membrane has relatively large pores, the majority of pore diameters being above 2 nm.

An improved method has now been found which results in hydrophobic membranes, both supported and unsupported, having pores sizes in the subnanometer range, and having permeances for small molecules such as H₂, CO₂, N₂, O₂ and CH₄ and good separation factors for these gasses with respect to larger alkanes such as propane and butane, and for compounds such as SF₆. The process of the invention is characterised by a controlled hydrolysis in that the hydrolysis rate of the hydrocarbyl metal alkoxide is taken into account in the rate of sol formation of the metal oxide, by adding a substantial part of the hydrocarbyl metal alkoxide after part of the metal alkoxide has been allowed to hydrolyse. The controlled hydrolysis is defined in the appending claims.

The invention also relates to novel hydrophobic membranes having improved characteristics over the prior art membranes, especially an average pore size (diameter) and/or a majority of pore sizes below 2 nm, or even below 1 nm, and a hydrophobicity index (HI) for octane/water of at least 2, especially at least 2.5 or even 3 or higher. The hydrophobicity index is defined as the ratio of loading of the membrane with hydrophobic substance (octane) to the loading with water as described by Klein and Maier (*Angew. Chem. Int. Ed. Engl.* 35, (1996) 2230-2233; and by Weitkamp et al (*Proc. 9th*

Intern. Zeolite Conf. Montreal 1992, Von Balmoos et al Eds. (1993) 79–87). The membranes show high permeances for small molecules, and especially allow separation of small hydrophobic molecules from water or from other hydrophobic molecules, also in the presence of water (humid process streams). Larger molecules such as butane and methyl tert-butyl ether have permeances which are more than 20 times lower than those of the small molecules such as H₂, methane, methanol etc.

According to the process of the invention the larger part of the hydrocarbyl metal alkoxide is added after at least 20% of hydrolysis of the metal alkoxide has occurred. The percentage of hydrolysis occurred can roughly be considered equivalent with the percentage of the "normal" hydrolysis period that has lapsed, but more precisely it is the percentage of the total theoretical hydrolysis of metal alkoxide to metal (hydr)oxide. The total amount of hydrocarbyl metal alkoxide used means the total amount added to the hydrolysis system for the purpose of being incorporated into the membrane after hydrolysis. The larger part introduced after at least 20% of hydrolysis is at least 75% of the total amount, but especially essentially the total amount. It is further preferred that a substantial part, especially at least 50%, of the hydrocarbyl metal alkoxide is added only at a later stage, i.e. after at least 50% or even at least 70 or 80% hydrolysis of the metal alkoxide.

The terms metal oxide and metal (hydr)oxide are used interchangeably and denote any oxide, hydrated oxide, hydroxide or mixed oxide/hydroxide of any trivalent or higher-valent element from period 3 and higher periods and groups 3 and higher groups of the periodic table of elements, including e.g. Al, Si, Sc, Ti, V, Ge, Sn, Hf, Ce, as well as combinations thereof such as Si/Ti and Si/Zr.

In the term metal alkoxide as used herein, the metal is defined as above, whereas an alkoxide is understood to comprise the residue obtained by deprotonation of any organic molecule containing a hydroxylic group and an alkyl group; the hydroxyl group may directly be attached to the alkyl group, such as in the methanol, ethanol, propanol, isopropanol, butanol and the like, but also through a carbonyl group as in carboxylic acids (acetic acid, propionic acid and the like); the hydroxyl group may also be an enol tautomer of a ketone, especially a β -diketone or β -ketoester, such as acetyl-acetone (= 4-hydroxy-3-propene-2-one). Examples of metal alkoxides include tri-butoxyaluminium, tetraethoxysilane (TEOS), tetra-isopropoxysilane, tetrabutoxytitanium,

tripropoxytitanium acetoacetate, tributoxytitanium acetate, tetrabutoxyzirconium, tripropoxyzirconium, tetraethoxytin.

A hydrocarbyl metal alkoxide as used herein denotes a compound of a tri- or higher-valent metal as described above with at least one alkoxide group as defined above and at least one hydrocarbyl group which is bound to the metal with a bond which, under normal conditions (temperature below 100°C, pH between 1 and 13), is non-hydrolysable. Such a hydrocarbyl group can be any organic radical containing from 1 to 8 carbon atoms and the corresponding number of hydrogen atoms, such as methyl, ethyl, butyl, isooctyl, phenyl and benzyl. Small alkyl groups, i.e. with 4 or less carbon atoms, especially methyl and ethyl are preferred. Examples include methyl-triethoxysilane (MTES), phenyl-trimethoxysilane, diethyl-dipropoxytitanium, methyl-dibutoxyzirconium acetate, and the like.

The hydrolysis is carried out in an organic solvent such as ethers (tetrahydrofuran, dimethoxyethane, dioxane and the like), alcohols (methanol, ethanol, isopropanol, methoxyethanol and the like), ketones (methyl ethyl ketone and the like), amides etc. Alcohols, such as ethanol, are the preferred solvents. The hydrolysis is carried out in the presence of water and, if necessary, a catalyst. The amount of water to be used depends on the hydrolysis rate of the particular metal alkoxide and hydrocarbyl metal alkoxide, and the volume ratio of water to organic solvent can vary from e.g. 1:99 to 75:25. A catalyst may be necessary if hydrolysis in neutral water is too slow. An acid or a base can be used as a catalyst. For titania and zirconia sol preparation, a catalyst may not be necessary. For silica sol preparation the conditions as described by De Lange et al. (*J. Membr. Sci.* **99** (1995), 57-75) can be followed. The hydrolysis temperature can be between ambient temperature and the boiling temperature of the organic solvent. It is preferred to use elevated temperatures, in particular above 40°C up to about 5°C below the boiling point of the solvent, e.g. up to 80°C in the case of ethanol.

The drying and/or calcination of the precipitate is preferably carried out under an inert, i.e. non-oxidising atmosphere, for example under argon or nitrogen. The calcination temperature is at least 100°C, up to about 800°C, preferably between 300 and 600°C, using a commonly applied heating and cooling program. The porosity of the membranes can be tuned by selecting the specific metal (hydr)oxide precursor, the appropriate hydrolysis conditions, and the appropriate consolidation parameters (drying

velocity, rate and temperature of calcination). Higher temperatures typically result in smaller pore sizes.

Applications of the supported microporous hydrophobic membrane of the invention are especially advantageous in humid process streams, where several problems are encountered by the moisture such as pore blocking and deterioration (e.g. hydro-thermal degradation). Furthermore, hydrophobic species can be separated from hydrophobic and hydrophilic ones in liquid separation and gas separation, and especially in pervaporation. Isomer mixtures, such as butene/isobutene and p-/m-/o-xylene can also be efficiently separated into the individual components. Other useful applications are in air cleaning processes for the removal of dust particles or volatile organic compounds without the membrane being blocked by water.

Example

1. Standard membrane preparation

'Standard' (hydrophilic) silica membranes (Si(400)) were prepared by the sol-gel method for comparison purposes. A silica sol was prepared by catalysed hydrolysis and condensation of TEOS in ethanol. A mixture of acid and water is carefully added to a mixture of TEOS and ethanol under vigorous stirring. The sol solution was prepared by refluxing the mixture at 60°C for 3 hours. Membranes were made by dipping a supported γ -alumina membrane in a diluted sol solution, followed by thermal treatment (De Vos and Verweij, *J. Membrane Sci.* **143** (1998) 37-51).

2. Hydrophobic membrane preparation

In order to make the silica more hydrophobic, methyl-tri-ethoxy-silane (MTES) is incorporated at a certain stage of sol preparation. The hydrolysis/condensation rate of MTES is about 7 times faster than that of TEOS. Therefore a 'standard' silica sol solution preparation was started and MTES was added after at least 6/7 of the usual total reaction time. If MTES was added too fast, hydrolysis and condensation took place for a longer time resulting in bulkier polymers which become visible through light-scattering in the sol solution, which gives rise to larger pores in the membrane (> 2 nm).

The complete sol preparation procedure for hydrophobic membranes was as follows: TEOS was mixed with ethanol. A mixture of catalyst (acid) and water was added under vigorous stirring. After the addition was complete, the reaction mixture was heated for 2.75 hours at 60°C under continuous stirring. This reaction mixture had a

molar ratio (based on unreacted components) TEOS/ethanol/water/acid of 1/3.8/6.4/0.085 according to the 'standard' recipe of silica sol preparation (see: De Lange et al., *J. Membrane Sci.* **99** (1995) 57–75). MTES was mixed with ethanol in the ratio of 1/3.8 and the mixture was added to the TEOS reaction mixture after 2.75 h heating. The MTES/TEOS reaction mixture obtained was heated for 15 minutes at 60°C. The mixture then had a molar ratio MTES/TEOS/ethanol/water/acid (based on unreacted components) of 1/1/7.6/6.4/0.085. The reacted mixture was then cooled and diluted 19-fold with ethanol to obtain the final dip solution. After dipping the membranes are calcined at 400°C for 3 hours in pure nitrogen with a heating and cooling rate of 0.5°C/min. The membranes obtained in this way are referred to below as "MeSi(400)membranes". A similar procedure could be followed using titanium(IV) isopropoxide or titanium(IV) methoxide in combination with MTES as reactants to obtain a hydrophobic Ti/Si system.

3. Unsupported silica materials

Unsupported microporous silica material was made by evaporation of 60 ml of the dip solution in a 10 cm petri dish at room temperature, the unsupported silica material being obtained overnight. This was done for both 'standard' sols and sols to which MTES was added, referred to as Si(400) and MeSi(400) respectively. The silica materials were calcined at 400°C for 3 hours with a heating and cooling rate of 0.5°C/min in air for Si(400) and in pure nitrogen for Me Si(400).

4. Membrane characterisation

Morphological characterisation of hydrophobic silica membranes is accomplished by Field-Emission Scanning Electron Microscopy (FE-SEM). The FE-SEM recordings revealed a crack-free continuous layer.

Thermogravimetric analysis (TGA) was performed on Si(400) and MeSi(400) unsupported material to obtain a qualitative indication of the amount of hydroxyl groups in the silica material. Both samples were stored at room temperature and normal relative humidity before measurement. The experiments were performed in a pure N₂ stream with a water and oxygen content <5 ppm and a heating rate of 1°C/min to 800°C. For the MeSi(400) sample this resulted in the absence of mass release until 500°C, while for Si(400) a decrease in mass at about 100°C was observed due to the release of physically adsorbed water and above 100°C due to the release of hydroxyl groups.

The hydrophobicity of the unsupported membrane material was determined by measuring the hydrophobicity index $HI = x_{octane}/x_{water}$ as described by Klein and Maier (see above). The sample was dried first for 12 hours at 250°C under an Ar stream. After that an Ar stream, containing defined and equal concentrations of water and octane was used to load the sample until saturation at a temperature of 30°C. The breakthrough curves of the individual components were obtained by on-line gas chromatography. Numerical integration of the normalised breakthrough curves provided the loading of water (x_{water}) and octane (x_{octane}). After correction for the background behaviour of the total reactor, the hydrophobicity index HI was obtained as the ratio x_{octane}/x_{water} . The value thus determined for MeSi(400) was 3.0. The comparable value for non-hydrophobised Si(400) membrane was 0.3, so the MeSi(400) material is 10 times more hydrophobic. The hydrophobicity of the MeSi(400) membranes could be made visible by putting a drop of water on the membrane and observing the difference in contact angle. The contact angle was smaller for the Si(400) material.

The presence of methyl groups in the microporous structure was demonstrated with Infra-red spectroscopy. For that, a sample was made of 20 mg of unsupported membrane material plus 200 mg of KBr. The sample was heated under an Ar stream in the IR-cell at 400°C for 20 hours. The spectra were recorded at 30°C in the diffuse-reflectance mode. For the MeSi(400) material an additional peak at 1280 cm^{-1} was observed. Such a peak is characteristic for Si-C bonds.

Adsorption isotherms were determined by Ar and N_2 adsorption. Ar adsorption was performed at both liquid nitrogen and liquid argon temperature (77K and 87K, respectively). The pore diameter determined for MeSi(400) was about 7 Å and for Si(400) it was about 5 Å. The pore size distribution for MeSi(400) is larger than for Si(400).

The performance of the membranes was determined by single-gas permeance experiments in a dead-end set-up. Prior to the permeance experiments the membranes were dried at 300°C under a He stream to remove any moisture from the pore structure of both the γ -alumina intermediate layer and the silica top layer. All characterisations were done for both Si(400) and MeSi(400). The removal of moisture from the pore structure took only 30 minutes for the MeSi(400) membranes, while it takes 3 to 4 hours for the Si(400) membranes. The moisture removed from the MeSi(400) membranes was probably present in the hydrophilic γ -alumina later. Permeance of several gasses at

different temperatures are given in table 1.

Table 1
Permeances of membranes in $10^{-7} \text{ mol.m}^{-2} \cdot \text{sec}^{-1} \cdot \text{Pa}^{-1}$

gas	MeSi(400)		Si(400)	
	100°C	200°C	100°C	200°C
H ₂	23	22	11	17
CO ₂	5	4	2.9	2.3
O ₂	4	3.5	0.74	0.88
N ₂	2.8	2.6	0.19	0.27
CH ₄	2.7	2.7	0.015	0.031
SF ₆	0.01	0.01	0	0

Claims

1. A process for producing an inorganic microporous hydrophobic membrane comprising hydrolysing a metal alkoxide in the presence of a hydrocarbyl metal alkoxide having at least one non-hydrolysable group in an organic solvent to produce a metal (hydr)oxide sol, and precipitating metal (hydr)oxide from said sol and drying the precipitate, *characterised* in that at least 75 % of the amount of the hydrocarbyl metal used is introduced into the solvent occurs at least 20% of the metal alkoxide has been hydrolysed to metal (hydr)oxide.
2. A process according to claim 1, *characterised in that* at least 50% of the amount of hydrocarbyl metal alkoxide is introduced into the solvent after 70% of the metal alkoxide has been hydrolysed.
3. A process according to claim 2, *characterised* in that at least 75% of the amount of hydrocarbyl metal alkoxide is introduced into the solvent after 80% of the metal alkoxide has been hydrolysed.
4. A process according to any one of claims 1-3, wherein the hydrolysis is carried out at a temperature between 40°C and the boiling point of the solvent.
5. A process according to any one of claims 1-4, wherein the metal (hydr)oxide is precipitated onto a porous inorganic support.
6. A process according to any one of claims 1-5, wherein the molar ratio of metal alkoxide to hydrocarbyl metal alkoxide is from 5:95 to 95:5, preferably from 20:80 to 80:20.
7. A process according to any one of claims 1-6, wherein the dried precipitate is calcined at a temperature between 100 and 800°C, especially between 300 and 600°C, preferably in an inert atmosphere.
8. A process according to any one of the preceding claims, wherein the metal alkoxide comprises a tetraalkoxysilane, tetraalkoxytitanium, tetraalkoxyzirconium or a mixture thereof and/or the hydrocarbyl metal alkoxide is an alkyltrialkoxysilane.
9. A process according to claim 8, wherein the metal alkoxide comprises tetraethoxysilane and the hydrocarbyl metal alkoxide is methyl triethoxysilane.

10. Microporous hydrophobic inorganic membrane obtainable by the process of any one of claims 1-9, having an average pore size of less than 2 nm and a hydrophobicity index octane/water of at least 2.
11. Use of a microporous membrane according to claim 10, or obtained by the method according to any one of claims 1-9, for separating components from mixtures containing them.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/NL 99/00333

A. CLASSIFICATION OF SUBJECT MATTER IPC 6 B01D71/02		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 6 B01D B01J C01B C04B		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 395 954 A (R. SORIA ET AL.) 7 March 1995 (1995-03-07) the whole document ---	1
A	SMAIHI M ET AL: "ORGANIC-INORGANIC GAS SEPARATION MEMBRANES: PREPARATION AND CHARACTERIZATION" JOURNAL OF MEMBRANE SCIENCE, vol. 116, no. 2, 7 August 1996 (1996-08-07), pages 211-220, XP000730132 the whole document -----	1
<div style="display: flex; justify-content: space-between;"> <input type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex. </div>		
<div style="display: flex;"> <div style="flex: 1;"> <p>* Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="flex: 1;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </div> </div>		
Date of the actual completion of the international search <div style="text-align: center;">26 August 1999</div>		Date of mailing of the international search report <div style="text-align: center;">03/09/1999</div>
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer <div style="text-align: center;">Devisme, F</div>

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/NL 99/00333

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5395954 A	07-03-1995	FR 2693727 A	21-01-1994
		CA 2100802 A	21-01-1994
		EP 0580487 A	26-01-1994
		JP 6157766 A	07-06-1994
<hr/>			